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THE DECOMPOSITION OF AMMONIA

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Distribution

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At the request of Dr. T. S. Laszlo, the literature was surveyed for reference to the decomposition of ammonia as a function of temperature, water vapour present, and catalyst used. Iron, nickel and ceramic catalysts were of special interest.

Using Chemical Abstracts, Volumes 41, 1947 - 69, 1968, all entries under the keyword "Ammonia" were searched.

Relevant abstracts were reproduced directly from the source and are listed in chronological order of original publication. Within each year, abstracts are alphabetically listed according to lead author.

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1943

Chem. Abstr. 41, 3356f, 1947.

The relation between the α-γ-transformation of iron-nickel alloy and the velocity of catalytic decomposition of ammonia gas when this alloy is used as catalyst. II. Effect of the nickel content of the alloy. Tadaibumi Koyano. *J. Chem. Soc. Japan* 64, 1306–8(1943); cf. *C.A.* 41, 2863*h*. —The catalytic activity of the alloy (Ni = 15%, Fe = 85%) for the decompn. of NH_3 was studied at various temps. Hysteresis is observed; i.e. there is a difference in the catalytic activity during the rise and fall of temp. A tentative explanation is given in the light of the lattice theory. III. Effect of the surface treatment of the alloy. *Ibid.* 1480–5.—The effect of various treatments of the Ni-Fe alloys (Ni = 10, 15%) upon the catalytic activity for the decompn. of ammonia gas was studied. When the alloys are washed with 15% HNO_3 and reduced at 800° by means of H_2, no effect of α-γ-transformation is observed in the catalytic activity. When the alloys are oxidized by oxygen and then reduced at 800° by means of H_2, hysteresis of the catalytic activity is observed. T. Katsurai

1947

2. Chem. Abstr. 43, 2744d, 1949.

The preparation and transformation of iron nitride. H. W. Kohlschütter and K. Jaenes. *Z. anorg. Chem.* 255, 73–8(1947).—The prepn. of the nitrides of Fe by reaction of Fe with NH_3 and the catalytic decompn. of NH_3 with the intermediate formation of Fe_2N are discussed. I. E. Campbell

3. Chem. Abstr. 42, 2501g, 1948.

Kinetics of synthesis and decomposition of ammonia on various catalysts. M. Temkin and S. Kiperman (Karpov Inst. Phys. Chem., Moscow). *J. Phys. Chem.* (U.S.S.R.) 21, 927–52(1947)(in Russian); cf. *C.A.* 36, 6292⁴.—The equation for the rate v of reaction, $v = k_1P_1(P_3^3/P_2^2)^{\alpha} - k_2(P_3^3/P_2^2)^{1-\alpha}$, in which P_1, P_2, and P_3 are the partial pressures of N_2, H_2, and NH_3, resp., and k_1, k_2, and α are const., is integrated by assuming the total pressure to be const. The energy of activation is expressed as a function of α. The best compn. of the gas mixt. is given by P_2:-$P_1 = 3\alpha$. The above equation is valid only when the system is not too far removed from the equil. state. Variations of the adsorbed amt. of N_2 may cause the decompn. of NH_3 to be a zero-order reaction at very low NH_3 concns. Consideration of earlier expts. shows that the equation is valid for various catalysts (Fe, Mo, W, U, Ce, Mn, Os, Ru, Cu, and Pt), that α usually is 0.5, and that the activation energy is almost independent of the nature of the catalyst. This proves that the reaction mechanism is identical on various catalysts. The rate of synthesis should depend on the degree of uniformity of the catalyst surface. 57 references. J. J. Bikerman

1948

4. Chem. Abstr. 43, 7312h, 1949.

Kinetics of the decomposition of ammonia on iron. J. Zawadzki and E. Pasternak. *Bull. intern. acad. polon. sci., Classe sci. math. nat.*, Ser. A., 1940–46, 119–22(1948) (in English); cf. *C.A.* 26, 3137.—Former conclusions regarding the constancy of resistance and temp. of Fe wire when it is used to decomp. NH_3 were investigated by a static and a dynamic method. Under the static conditions the same wire showed an increase of contact properties; this counteracted somewhat the opposite effect of diminishing concn. of NH_3 and the increasing concn. of H_2. Likewise a const. temp. in Fe wire did not result, since the resistance increased with an increasing concn. of NH_3. Because of opposing effects the reaction appeared to be of zero-order, though actually of first-order. Likewise a similar decompn. of NH_3 on W wire was shown to be of first-order. R. E. Dunbar

1949

5. Chem. Abstr. 44, 1313h, 1950.

Catalysis on nonuniform surfaces. G. D. Halsey, Jr. *J. Chem. Phys.* 17, 758–61(1949).—With NH_3 decompn. as an example, the kinetics of a heterogeneous reaction are discussed. On a continuously nonuniform surface, no single reaction step is the limiting one; on the optimum sites 2 reaction steps are equally slow. The expression for over-all velocity is developed, and solved exactly for the case of an exponential distribution of activation energies. It appears that if the distribution is broad, its exact shape is unimportant, but that a factor r, connected with the amt. of adsorption energy available for catalytic work, is important. For a broad distribution, the pressure dependence of the over-all rate is the same as the pressure dependence on the optimum sites. Because the position of the optimum depends on pressure, it cannot be assumed that the surface is "effectively uniform." The simplest of NH_3 kinetics is discussed, but it appears that on a nonuniform surface, much more extensive expts. than have been available are necessary to elucidate properly the kinetics of a reaction. L. J. E. Hofer

6. Chem. Abstr. 47, 5744g, 1953.

Magnetic properties of iron-carbon catalysts. S. L. Kiperman and M. I. Temkin. *Problemy Kinetiki i Kataliza* 6, 206–9(1949); cf. following abstr.—Carbon (from sucrose, burned at 700–800°) of sp. surface area 94 sq.m./g., was impregnated with ether solns. of Fe(CO)$_5$ and decompd. by the method of Klyachko-Gurvich and Kobozev (*C.A.* 36, 4013³); the catalyst had approx. the same catalytic activity for decompn. of NH_3. The magnetic susceptibility χ per 1 g. Fe was measured by the Gouy and the Curie-Chéneveau methods on catalysts with different Fe contents (different surface coverages α). If the Fe were present in the form of isolated atoms, as called for by the ensemble theory of Kobozev (*J. Phys. Chem.* (U.S.S.R.) 13, 1 (1939); 19, 48(1945)), the susceptibility should be $\chi = NB^2n(n + 2)/3kTA$, where N = Avogadro's no., B = Bohr's magneton, $n = 4$ = no. of unpaired electrons, A = at. wt., i.e. $\chi = 1.78 \times 10^{-4}$. Actually measured values, even at high α (up to 0.101) were considerably higher than the max. possible χ for paramagnetic Fe. It is, therefore, concluded that the Fe on C is ferromagnetic down to lowest α (0.00008); χ is not much different from the susceptibility of Fe in mech. mixt. with C. The fact that χ increases somewhat with decreasing α is taken as an indication that the size of the Fe crystals increases somewhat. The Fe crystals are made of no less than 1000 atoms. In the ensemble theory, this would require a migration range of about 10^7 at. areas. The migration range of the ensemble theory probably does not exist at all. N. Thon

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1949 (Continued)

7. Chem. Abstr. 49, 15416d, 1955.

Catalytic processes on nonuniform surfaces. M. I. Temkin. *Problemy Kinetiki i Kataliza, Akad. Nauk S.S.S.R.* 6, *Geterogennyi Kataliz* 54-65(1949).—By a numerical stepwise analysis of data on decompn. of SbH_3 by Stock and Bodenstein (cf. *C.A.* 1, 1950), it is shown that their equation matches the data better than does the I. Langmuir's equation; this indicates that the concept of a uniform surface does not apply. Simple Frumkin and Freundlich isotherms do not account for a limited no. of adsorption sites on the surface. An equation for the generalized surface-catalyzed reaction $A \rightarrow B$ is derived for the case where adsorption of B is negligible. Analogous to the concepts used by Brønsted in the acid-catalyzed reactions, it is postulated that $s = Gb^{\beta}$, where G and β are consts., s is defined as a kinetic const. in $A = sdt$, where A is the probability that the mol. adsorbed on the given site reacts in time dt, and b is the const. in the equation $\sigma = p/(p + b)$, where p is gas pressure, and σ the probability that the site is occupied. This postulate correlates the adsorptive and catalytically-kinetic characteristics of the surface sites. With this postulate all fractional exponents in the pressure term of the rate equation of the surface-catalyzed reactions can be explained on the basis of one of the 3 types of adsorption isotherms: logarithmic (Frumkin), Freundlich, and Freundlich's with admission of a neg. exponent in the power term. Kinetics of the catalytic decompn. of NH_3, the reaction of CO with H_2O vapor, and the oxidation of SO_2 are interpreted on basis of the proposed relations. Variation of the fractional exponent with method of prepn. of the same catalyst cannot be explained on the basis of mutual interactions of the adsorbed species alone; a nonuniformity of the surface must be assumed.

Andrew Dravnieks

1950

8. Chem. Abstr. 44, 6713c, 1950.

Nitrides and kinetics of decomposition of ammonia on iron catalysts. I. A. Legenchenko (Inst. Chem. Technol., Dzerzhinsk). *Zhur. Fiz. Khim.* 24, 311-20(1950).—Dry NH_3 was passed through Fe catalyst (11 g. in 2-3-mm. pieces) at 400-450°. The NH_3 in the outgoing gas was sepd. and detd., and the ratio N:H in the residual gas was detd. interferometrically. If this ratio R was less than 1:3, Fe nitride (I) formation took place, and the amt. of I formed could be calcd. from R. During one expt., the rate u of decompn. of NH_3 increased with time and became almost const. (in, e.g., 10 min.); simultaneously, the rate v of I formation decreased and became almost zero in 10-20 min. (when the rate of gas flow was 6-19 l./hr.). The decompn. of NH_3 and the formation of I take place on different surface patches. This was confirmed by adding H_2 to NH_3; this addn. (e.g., 33 mol. %) little affected u but reduced v to, e.g., one-half. Addn. of H_2O (e.g. 3 mol. %) lowered u and had nuclear effect on v but extended the time of I formation so that the final amt. of I formed was greater than in dry NH_3. Addn. of H_2O to NH_3 at a time when the catalyst already contained much I caused increase in R above 1:3, i.e. displacement of "chemically sorbed" N by H_2O. Decompn. of NH_3 can occur either directly or as a sequence: formation of I on inactive spots → migration of I to active spots → decompn. of I; poisons stop the migration.

J. J. Bikerman

1950 (Continued)

9. Chem. Abstr. 45, 5011d, 1951.

The catalytic decomposition of ammonia. IV. Decomposition by means of nickel. Shozo Miyazaki (Tokyo Inst. Technol.). *J. Chem. Soc. Japan*, Pure Chem. Sect., 71, 77-80(1950); cf. *C.A.* 45, 2759c, 4121*f*.—The decompn. of NH_3 gas on Ni metal was studied at 700-775°. The NH_3 pressure was 150-350 mm. Hg. The reaction is retarded by the H_2 gas produced in the reaction. The relation between the reaction rate and the NH_3 gas pressure is expressed by a J-type curve. The calcd. activation energy from these initial reaction velocities is 47.2 kcal. per mol. V. The equation of reaction rates. *Ibid.* 335-8.—A theoretical equation on the reaction rate was derived by statistical mechanics. The structure of the adsorbed or activated NH_3 gas mol. was discussed by comparing theoretical and empirical equations.

T. Katsurai

10. Chem. Abstr. 45, 6473a, 1951.

Catalytic decomposition of ammonia gas. VI. The equation of reaction rates. 2. Shozo Miyazaki (Tokyo Inst. Technol.). *J. Chem. Soc. Japan*, Pure Chem. Sect., 71, 372-3(1950); cf. *C.A.* 45, 5011*d*.—The theoretical relation between the NH_3 pressure and the reaction rates is derived by statistical mechanics. The structure of the adsorbed or activated NH_3 gas mol. is examd. in the light of the theory. VII. Decomposition on tungsten. *Ibid.* 424-6(1950).—The catalytic decompn. of NH_3 gas in the presence of W was observed at the temp. 730-810°, under the pressure 15 mm. Hg. The theoretical equations explain the observed relations between the reaction velocities and the NH_3 and H_2 gas pressures. The heat of activation and the heat of adsorption of NH_3 gas on W are calcd. They are 46.4 kcal./mol. and 26.6 kcal./mol., resp. VIII. Decomposition on molybdenum. *Ibid.* 483-5.—The thermal decompn. of NH_3 gas in the presence of Mo was observed in the NH_3 gas pressure range of 3-15 mm. Hg at 700-760°. The relations between the observed reaction rates and the gas pressures are represented by the theoretical equation (cf. Part VI, above). The activation energy and heat of adsorption of NH_3 gas on Mo are calcd. to be 45.7 kcal. $mol.^{-1}$ and 22.8 kcal. $mol.^{-1}$, resp.

T. Katsurai

11. Chem. Abstr. 46, 8480i, 1952.

The kinetics of decomposition of gases at metal surfaces. M. F. R. Mulcahy (Commonwealth Sci. Ind. Research Organisation, Melbourne). *Trans. Australian Inst. Metals* 3, 67-70(1950); *Australasian Engr.* Dec. 7, 1950, 27-8.—In this review of the theory of metal-gas surface reactions, the results of published expts. on the rate of deposition of C from CH_4 and of N from NH_3 are described briefly, together with a comparison of reaction rate with the diffusion rate in carburizing and nitriding processes. 29 references.

S. Mouy

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1951

. Chem. Abstr. 45, 5502d, 1951.

Catalytic capacity of sintered iron material. C. F. Hüttig, L. Zagar, and E. R. Honak. *Monatsh.* 82, 183-6(1951).—The energy of activation for the decompn. of H_2 by Fe is 22,600 cal. for Hametag Fe (reduced and sintered in H_2 stream) and 15,700 cal. for carbonyl Fe. It is independent of the degree of sintering and the sintering temp. The activity of the catalyzing centers in carbonyl Fe is superior, but Hametag Fe has more such centers. If Hametag Fe is reduced and sintered in a stream of NH_3, its catalytic activity is improved considerably.

Alfred M. Pommer

. Chem. Abstr. 46, 3383d, 1952.

The thermal decomposition of ammonia gas. XI. Decomposition of ammonia gas on various metals at low pressure. Shozo Miyazaki (Tokyo Inst. Technol.). *J. Chem. Soc. Japan*, Pure Chem. Sect., 72, 1-3(1951); cf. *C.A.* 45, 7864i.—The decompn. of NH_3 gas on W, Mo, Pt, and Ni was studied at 650–800° in the pressure range 0.5–1.0 × 10^{-4} mm. Hg. In each case the retarding action disappears and the relation between pressure and vol. is represented as the 1st-order reaction with the lowering of pressure.

T. Katsurai

1952

hem. Abstr. 46, 10807i, 1952.

Application of the Temkin kinetic equation to ammonia nthesis in large-scale reactors. D. Annable (Imperial hem. Inds. Ltd., Billingham, Engl.). *Chem. Eng. Sci.* 1, 5–54(1952).—The fitting of the Temkin kinetic equation plant data obtained at temps. of 370–550° and at pressures of 245 and 360 atm. was made to find a measure of atalytic activity and to provide a means of estg. the best ractical reaction conditions. The apparent activation nergy for NH_3 decompn. is 45,800 cal./mol. at 245 atm. nd 47,000 cal./mol. at 360 atm., and the reaction velocity onst. for the decompn., as detd. from the plant data, conformed well with the Arrhenius equation.

C. MacK.

1953

. Chem. Abstr. 48, 11679c, 1954.

Decomposition of ammonia over doubly promoted iron talysts. I. Haruo Kobayashi and Osumu Nishijima (okkaido Univ., Sapporo). *J. Chem. Soc. Japan, Ind. hem. Sect.* 56, 587–9(1953).—The rate of decompn. (I) of H_2 was measured for several kinds of Fe-Al_2O_3-K_2O catasts at 380–535°. The variation of I with the concn. of H_2 in mixed gas showed 3 steps, and an interpretation is tried that the stepwise progress of I is attributed to talytic centers of Fe, Fe_4N, and Fe_2N + Fe_4N, which are rmed progressively on catalyst surface with NH_3 concn.

Katsuya Inoaye

1953 (continued)

16. Chem. Abstr. 49, 13059d, 1955.

Catalytic corrosion. S. Z. Roginskii, I. I. Tret'yakov, and A. B. Shekhter. *Doklady Akad. Nauk S.S.S.R.* 91, 881–4(1953).—Corrosion of metals inducing catalytic reactions is called catalytic corrosion. To det. the causes of this corrosion the catalytic decompn. of NH_3 in the presence of Fe, Cu, and Pt was investigated. This reaction is endothermic and thus the effect of local heating as a cause of corrosion is eliminated. Electron micrographs of these metals after having catalyzed the decompn. of NH_3 reveals that: in the case of Fe the marks of polishing disappear after 10 min. at 625° and the surface becomes covered with a porous substance with no definite cryst. structure; for Cu, 1.5 hrs. at 800° is required before the polishing scratches disappear, revealing intergranular boundaries; with Pt the same effect is achieved after 7 hrs. at 900°. The action of N or H separately does not affect Fe and Cu, but on Pt there appears a modification of the surface, which can be removed by heating, however. Three possible causes of this corrosion are put forward: (1) increase of mobility of surface atoms induced by the catalytic reaction and the use of part of its free energy either directly as excitation energy or indirectly as energy of formation of surface nitrides; (2) effect of sorption of gases on mobility not directly connected with catalysis, for example, sorption of NH_3 or H; (3) formation of new phases in the conditions of catalysis.

N. Goldowski

1954

17. Chem. Abstr. 49, 13748f, 1955.

Kinetics of synthesis and decomposition of a current of ammonia over iron catalysts. M. T. Rusov and Ts. V. Pevzner (L. V. Pisarzhevskii Inst. Phys. Chem., Acad. Sci. Ukr. S.S.R., Kiev). *Zhur. Fiz. Khim.* 28, 1628–37 (1954); cf. Temkin and Kiperman, *C.A.* 42, 2501g.—The rate of decompn. of a current of NH_3 at various temps. and pressures in the presence of porous Fe granules (diam. about 9 mm.) (I) as well as Fe foil (II) was measured in a described and illustrated app. in which the reaction took place in a Mo-glass or SiO_2 vessel contg. a thermocouple. Results are tabulated and graphed. The reaction rate in the temp. range 290–500° is detd. by diffusion exchange in the I. The reaction proceeds only in transitional kinetic regions and is confined to those portions of the I which lie within 2 mm. of the surface; the apparent activation energy (E) is 17.5 to 21.0 kcal./mole. Over II at temps. from 540 to 740° the reaction proceeds in the external kinetic region; E is 54 kcal./mole. Above 740° transition to the external diffusion region occurs. The transitional regions observed with I do not appear with II. Measurements of the rate of formation of NH_3 in a current of mixed N and H over I at temps. below 390° show that this synthesis proceeds in the internal kinetic region; the E of decompn. is 61.0 kcal./mole. At optimum temps. the rate of NH_3 formation is detd. by diffusion exchange in the I; the reaction proceeds in transitional regions.

J. W. Lowelberg, Jr.

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1954 (continued)

8. Chem. Abstr. 50, 1435b, 1956.

Kinetics of decomposition of ammonia over catalysts of different kinds. M. T. Rusov and Ts. V. Pevzner (L. V. Pisarzhevskii Inst. Phys. Chem., Kiev). *Zhur. Fiz. Khim.* 28, 1765–9(1954); cf. *C.A.* 49, 13748*f*.—The rate of decompn. was measured of NH_3 (I) in a mixt. of N and H with 10–14% I at initial I partial pressures around 100 mm. and temps. between 700 and 900° in a described and illustrated SiO_2 vessel (designed to minimize diffusion effects) without added catalyst as well as in the presence of Cu or Fe foil. Data on I partial pressure after 2 hrs. reaction time are graphed. The activation energy (E) for decompn. of I in contact only with SiO_2 is 38.2 kcal./mole; the reaction proceeds only above 720°. Over Cu E varies with I concn. from 57.6 to 62.0 kcal./mole. Over Fe the reaction proceeds above 740° in the external-diffusion region. The specific rate consts. (k) for Fe, Cu, and SiO_2 and their frequency factors (Z) are tabulated for the temp. range 715–60°. At 760° (I partial pressure 0.144 atm.) values of k for Fe, Cu, and SiO_2 are 4.220, 2.420, and 0.00683 moles/l.-sec., resp., whereas the corresponding values of Z are 1.09×10^{12}, 1.08×10^{12}, and 7.84×10^{5}, resp. J. W. Loweberg, Jr.

1955

9. Chem. Abst. 49, 15412c, 1955.

Decomposition of ammonia by doubly promoted iron catalyst. II. Kinetics of the decomposition. Haruo Kobayashi (Hokkaido Univ., Sapporo). *J. Chem. Soc. Japan*, Ind. Chem. Sect. 58, 490–3(1955); cf. *C.A.* 48, 11679*c*.—A theoretical examn. of the rate of decompn. of I_2 on the surfaces of iron catalysts has revealed that the rate-controlling factor is the desorption of N from catalyst surfaces. The rate of decompn. of NH_3 (U) in unit length of catalyst layer is expressed by the following equation: $U = k[x^2/(1-x)^2]^{1-n}$, where x is the mol. ratio of NH_3 in the gas, k is a const., and n is another const. concerning the state of sorption of N on the catalyst surface and takes the corresponding value between 0 and 1. The data reported in the preceding work (*loc. cit.*) were analyzed by the proposed formula and were discussed in relation to the different areas on catalyst surface which are occupied by different kinds of compds. between Fe and N. The results of earlier workers were also compared and discussed. It has been also suggested that the rate of desorption of N is basically similar to the rate of decompn. of Fe-N compds. on surfaces. The type of equations expressing the decompn. rate of NH_3 varies with the reaction conditions and (or) the kind of catalyst. Katsuya Inouye

0. Chem. Abstr. 54, 18907c, 1960.

Apparatus for the catalytic dissociation of ammonia. Société chimique de la grande paroisse (Azote et produits chimiques) (by Alfred Normand). Fr. 1,093,755, Oct. 22, 1955. An app. is described for the catalytic decompn. of gaseous NH_3 which is designed to minimize the deterioration (by nitriding) of metal parts and of the catalyst. This is accomplished by control of the temp. and the NH_3 content of the gas and by selection of materials of construction. Two catalysts are used. The 1st catalyst, operating at 700°–900°, is of low activity, resistant to nitriding, and consists of a refractory material, such as porous porcelain, impregnated with metal oxides, such as NiO, MoO_2, or CoO. This catalyst decomp. a large portion of the NH_3 in the feed gas. The 2nd catalyst, operating at 450–600°, is an active, reduced Fe oxide catalyst which lowers the NH_3 content to substantially the equil. value. For parts of the app. at >300° and brought into contact with gas rich in NH_3, high-alloy steels (Ni >25%), or high in Ni and Co, or Inconel are used. The inlet gas to the reactor is dild. with N and H recycled from the outlet with an injector by using gaseous NH_3 at 5–10 atm. as the motive fluid. J. T. Banchero

1955 (continued)

21. Chem. Abstr. 53, 2508f, 1959.

Microscopic studies on fused catalysts for ammonia syntheses. IV. Decomposition of ammonia over two different constitents. Yoshio Osumi (Kyoto Univ.). *Bull. Chem. Soc. Japan* 28, 156–61(1955); cf. *C.A.* 52, 5081*b*.—An unreduced Fe synthetic NH_3 catalyst promoted with K_2O or K_2O and Al_2O_3 was sepd. into 2 different sorts of powders (*A* and *B*). Their catalytic activities for decompg. NH_3 mixed with H were studied at atm. pressure by a specially devised flow method. It was found that *A* powder was more active than *B* between the temp. of 400 and 500° for gas mixts. of various compns. The liability to the poisoning effect of H_2O vapor or CO was equal. Heating both powders to 740° for 1 hr. had no effect. At 830° for 1 hr. *B* powder became less active and *A* powder also became less active, but soon recovered in the course of a run. The activity of a K_2O-free Al_2O_3-promoted catalyst was not affected by adding a small amt. of K_2O-rich *B* powder before reduction.

1956

22. Chem. Abstr. 51, 3256f, 1957.

The kinetics of the decomposition of ammonia on iron. G. M. Schwab and R. Krabetz (Univ. Munich, Ger.). *Z. Elektrochem.* 60, 855–9(1956); cf. Temkin and Pyzhev, *C.A.* 35, 7273⁹.—The decompn. of NH_3 on a nonactivated Fe was measured by a quasistatistical method in the region of low pressure. The kinetics of Temkin and Pyzhev is essentially confirmed. H. H. Jaffé

1957

23. Chem. Abstr. 51, 18512a, 1957.

Hydrogen-nitrogen mixture by thermal decomposition of ammonia. Stockholms Superfosfat Fabriks A/B (W. A. Backlund, inventor). Swed. 157,917, Feb. 26, 1957. NH_3 is led over a catalyst at a raised temp. (650°), so that the outgoing proportion of unchanged NH_3 is less than 0.02 vol. %. The catalyst consists of Al oxide in grain size coated with a layer, obtained by the reduction of oxides of Fe or one or more of the metals Cu, Co, Mn, Cr, or Ni. The catalyst is obtained by heating Al oxide grains with a soln. of the above-mentioned metals; the grains are dried slowly and then treated with H. During use nitrides are formed in the surface layer by decompn. of NH_3; this makes the catalyst more solid. Torsten Jakobson

24. Chem. Abstr. 53, 38h, 1959.

Mechanism of catalyzed decomposition of ammonia in the presence of doubly promoted synthetic catalyst. I. Decomposition rate. Juro Horiuchi and Isamu Toyoshima. *J. Research Inst. Catalysis, Hokkaido Univ.* 5, 120–4(1957).—Under steady-state conditions (in the absence of turbulence, diffusion, and inhomogeneity of temp.) and flow rates, the rate of decompn. of NH_3 (Uc) with a reduced doubly promoted Fe catalyst is given by: $Uc = [dv^4/d(1/N)]/V(1 + Yc^4)^2$, where $N = 2N_A + N_H$, y^4 = the observed fraction of NH_3 outflow rate over total outflow rate; V = the vol. of catalyst bed; N_A and N_H = the inflow rates of NH_3 and H, resp. Deviations due to turbulence and diffusion and to temp. inhomogeneity are theoretically analyzed with corrected values for Uc given as a function of temp. and mol. fraction of NH_3. Joseph Harris

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1957 (continued)

5. Chem. Abstr. 52, 894e, 1958.

Mechanism of some simple chemical reactions proceeding under the influence of ionizing radiations. S. Ya. Pshezhetskii and M. T. Dmitriev. *Uspekhi Khim.* 26, 725–67(1957). —Review of radiation-produced reactions involving H, H or T mixts. with CO, H-CuO, O, formation of O_3, decompn. of H_2O, decompn. of H_2O_2, CO, CO_2, N_2, N_2–O_2, decompn. of N oxides, formation of NH_3, decompn. of NH_3, formation of hydrazine, decompn. of hydrazine. A brief discussion of ionization and excitation processes in these reactions is given; 215 references through 1956. G. M. Kosolapoff

6. Chem. Abstr. 51, 10876f, 1957.

Hydrogen-nitrogen mixtures by decomposition of ammonia. John C. Upton and Ralph L. Robinson (to Imperial Chemical Industries Ltd.). Brit. 768,091, Feb. 13, 1957. An improved catalyst is described for use in NH_3 cracking app. for production of H and N for metallurgical and other purposes. Thus, the catalyst chamber is filled with pellets of Ni supported on α-Al_2O_3 (Ni content 10% by wt.). The chamber (Ni-Cr-Fe alloy) is indirectly heated to maintain a catalyst temp. of 900°. NH_3 is passed through at a rate of 400 vols./vol. of catalyst-filled space/hr. With this arrangement, the NH_3 content of the cracked gas is <0.015% by vol. After 10,000 hrs., no pressure-drop increase through the chamber is noted. The improved catalyst is not attacked by NH_3. It is more efficient than other Ni catalysts under identical operating conditions. It does not spall or sinter even at 1200°. It permits a moderately low and wide range of operating temps., and it may be used over very long periods without apparent deterioration. The catalyst is prepd. by conversion of Al_2O_3 to the α form by heating for 2–3 days at 1000–450°. It is held at the higher temp. for the last 8 hrs., cooled slowly in a kiln for another 2–3 days, and impregnated with Ni sulfate soln. It is drained, dried at 120°, and calcined in air for 4 hrs. at 450° to decomp. the nitrate to the oxide. Finally, metallic Ni is formed by reduction with H. T. P. G.

1958

7. Chem. Abstr. 52, 17639d, 1958.

Dissociation of ammonia. B. M. Estrin. U.S.S.R. 111,854, May 27, 1958. NH_3 is catalytically dissocd. in the presence of a metal e.g., Fe or Ni, deposited on a carrier of Al_2O_3. The catalytic activity is increased by adding Mg to the compn. of the catalyst. M. Hoseh

3. Chem. Abstr. 53, 11968f, 1959.

Mechanism of catalyzed decomposition of ammonia in the presence of a doubly promoted synthetic catalyst. II. Analysis of experimental results for the rate-determining step. Juro Horiuchi and Isamu Toyoshima (Hokkaido Univ., Sapporo). *J. Research Inst. Catalysis, Hokkaido Univ.* 6, 68–87(1958); cf. *C.A.* 53, 38*i*.—In the catalyzed reaction $2NH_3 = N_2 + 3H_2$, the rate-detg. step is: $NH_{3ads.} \rightarrow N_{ads.} + H_{ads.}$ The catalyzed decompn. rate was statistical-mechanically formulated according to the generalized theory of reaction rates (cf. *C.A.* 43, 6494*c*) as a function of NH_3 mole fraction and temp., ignoring all adsorptives but $N_{ads.}$, as confirmed by analysis of exptl. data of adsorption. The formula thus obtained for each of 2 possible rate-detg. steps was fitted to exptl. results (*C.A.* 53, 38*i*) with adjustable parameters, i.e. the no. G_1 of sites S for the crit. complex of the rate-detg. step per unit area of catalyst surface, the partition function Q_{N_2} of gaseous N_2, and the heat ΔX_{N_2} of dissociative adsorption of N_2. The result was that the crystallographic G_1 and spectrographic Q_{N_2} of 10^{15} and 10^{16}, resp., as well as the exptl. value of ΔX_{N_2} of 37 kcal./mol. were reproduced solely in the case when $NH_{3ads.} \rightarrow N_{ads.} + H_{ads.}$, with S consisting of 2 adsorption sites for each N adsorbed. M. D. Scheer

1958 (continued)

29. Chem. Abstr. 53, 3858b, 1959.

Catalytic decomposition of ammonia on evaporated iron films. S. R. Logan, R. L. Moss, and C. Kemball (Queen's Univ., Belfast, Ire.). *Trans. Faraday Soc.* 54, 922–30 (1958); cf. *C.A.* 46, 3318*b*.—The decompn. of NH_3 in NH_3–H_2 mixts. was followed by mass spectrometry. With small NH_3 content, initial rates to H_2 and N_2, without apparent loss of N_2 to the catalyst, gave an activation energy of 38.8 kcal./mole and were proportional to $p_{NH_3}^{0}p_{H_2}^{-1}p_{N_2}^{0}$. Reaction mixts. having a higher NH_3 pressure reacted with Fe to form Fe_4N, confirmed by x-ray diffraction analysis. Activation energies for the formation of the nitride phase were 38, decompn. 38.6, and hydrogenation 14 kcal./mole. Desorption of N_2 was the rate-detg. step. in NH_3 decompn. Where Fe_4N was formed, the effect of temp. on the rate of production of N_2 showed 3 distinct regions corresponding to decompn. of NH_3 on Fe, on a surface which was becoming increasingly nitrided, and finally on an Fe_4N surface. V. R. D.

30. Chem. Abstr. 55, 3262e, 1961.

Mechanism of the catalytic decomposition of ammonia. Miklós Magyar (Univ. Chem. Ind., Veszprém, Hung.). *Veszprémi Vegyipari Egyetem Közleményei* 2, 241–6(1958).—The decompn. of NH_3 on W and Fe catalysts was studied. On a W catalyst, the reaction proceeds as follows: $NH_3 + W = W\text{-}N + 1.5H_2$ and $W\text{-}N = 1.5\ N_2 + W$. The 1st reaction is very fast; thus, the over-all reaction rate is detd. by the surface recombination rate of the N atoms. Emmett's hypothesis (*Catalysis*, 1954, p. 141 (*CA* 48, 3784*a*)) regarding this process was confirmed. On a Fe catalyst, similar processes were found to take place. G. J. Ernyei

31. Chem. Abstr. 53, 13452i, 1959.

Catalytic decomposition of ammonia. L. Osipov, F. Ošis, and I. Kimene. *Latvijas Valsts Univ. Kim. Fak., Zinātniskie Raksti* 22, No. 6, 101–6(1958).—The reaction $2\ NH_3 = N_2 + 3\ H_2$ was studied on the following Fe-contg. catalysts: Fe chips, Fe silicide (I), activated I, and magnetite (II). This reaction was further studied by using as catalysts silicate bricks, MgO, and a synthetic product prepared from $K_4Fe(CN)_6$ and $Al(NO_3)_3.9H_2O$ which contained various amts. of K_2O, Al_2O_3, and Fe_2O_3. The decompn. was studied at 600, 700, 800, and 900°. Of all the materials, a II mined in the Ural Mountains was the most active; it decompd. the NH_3 noticeably at 600°. 17 references. Werner Jacobson

32. Chem. Abstr. 56, 3132d, 1961.

Decomposition of ammonia in a fluidized bed with iron catalyst. Pál Szolcsányi, Ferenc Bodó, and Antal Pásztor (Univ. Chem. Ind., Veszprém, Hung.). *Veszprémi Vegyipari Egyetem Közleményei* 2, 65–8(1958).—The app. described (cf. following abstr.) was used. The catalyst employed was Fe, as used in industrial NH_3 synthesis, of 0.20-mm.-diam. particle size. Feed rates were 0.2–5.0 l/min., temp. range was 450–500°. The activity of the fluidized bed was appreciably larger than that of the stationary bed. In a stationary bed the direction of flow (whether up or down) made no difference in the results. The av. conversion rate increased with an increasing feed rate. For any given bed, a sudden increase in activity occurred always at the same feed rate; this coincided with the change from the stationary to the fluidized state. G. J. Ernyei

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1958 (continued)

3. Chem. Abstr. 53, 12809e, 1959.

Mechanism of catalyzed decomposition of ammonia in the presence of doubly promoted synthetic catalyst. III. Hysteresis of the decomposition rate. Isamu Toyoshima and Juro Horiuchi (Hokkaido Univ., Sapporo). *J. Research Inst. Catalysis, Hokkaido Univ.* 6, 146–60(1958)(in English); cf. *C.A.* 53, 11968*f*.—H–NH_3 mixt. of different definite compns. was allowed to flow through a catalyst bed used in a previous expt. (*C.A.* 53, 2884), at 487° and 1 atm. total pressure, and the resulting per cent (R) of NH_3 decompn. at the steady state finally attained was observed similarly as in the previous expt. keeping the inflow rate (N_A) of NH_3 at 70 cc./min. and successively increasing or decreasing that (N_H) of H from one to the other observation. The present expts. were made in the same app. and catalyst bed as previously used (*loc. cit*). Having thus kept check with activity of the catalyst, the catalyst was now subjected to preliminary treatment with pure H at 550° for 4 to 5 hrs., and then the observation of the hysteresis was started by lowering the temp. of the catalyst to 487° and by switching the gas flow to that of NH_3–H mixt. of specified compn. Each run of a definite compn. of inflow gas was continued for 4 to 100 hrs. until the outflow rate (N'_A) of NH_3 remained perfectly const., when the inflow gas was switched to other compn. by increasing or decreasing N_H and fixing the N_A of NH_3 at 70 cc./min. throughout. The R at the latter steady state finally attained for each const. compn. of the inflow gas was then plotted against the ratio of N_H/N_A. The points lie reproducibly on a single curve that descends monotonicly with increase of N_H/N_A, as long as the runs were started at N_H/N_A greater than 4 and then conducted at N_H/N_A kept above 1.5 throughout. As N_H/N_A was decreased below 1.5, R continued to decrease for a long time down to a const. value appreciably lower than R of the foregoing runs at higher N_H/N_A. At $N_H/N_A < 1.5$ it took 67 hrs. for R to become const. which was then kept const. for further 30 hrs. On decreasing N_H/N_A further, R rose, until $N_H/N_A = 0$. Initially the outflow rate of NH_3 exceeded its inflow rate. This excess outflow of NH_3 decreased rapidly to vanish within the 1st 20 min. of the observation, its R being attained after 16 hrs. and kept for a further 12 hrs. The similar excess was observed at the 2nd cycle of tracing the hysteresis, when the value of N_H/N_A was switched from 1 to 4. After the above detn. of N_H/N_A of 0 and 1, the inflow rate of gas mixt. of const. compn. was varied in each case just as in the previous work. Total results indicate that R reveals a stable hysteresis. The hysteresis was satisfactorily accounted for on the basis of a slight modification of the mechanism concluded in the former paper and of the known phase equil. of the Fe–N system and shown to defy the rate-detg. step of the recombination of adsorbed N atoms in accordance with the previous conclusions. R. E. Dunbar

1959

. Chem. Abstr. 54, 23636g, 1960.

Estimated upper limits to the half-life of thermal decomposition of ammonia, hydrogen, methane, and propane. Dudley R. Herschbach. *U.S. At. Energy Comm.* LAMS-1954, 30 pp.(1959).—The upper limit was estd. for the ½-time of dissocn. at 100 atm. for NH_3, CH_4, and C_3H_8 at 1300°K. In each case a unimol. reaction in the homogeneous gas phase was chosen as most suitable. Slater's theory was used to est. the necessary frequency factors. The upper limits to the ½-time for dissocn. range from 3×10^{-7} to 5×10^{-5} sec. Extrapolation of decompn. rate data obtained at 1600° and 1 atm. pressure gives smaller values for the ½-time of dissocn. From *Nuclear Sci. Abstr.* 13, Abstr. No. 20891(1959). K. L. C.

1959 (continued)

35. Chem. Abstr. 54, 11622i, 1960.

Relation between catalytic activity and weight of metal films used for the decomposition of NH_3. S. R. Logan and C. Kemball (Queen's Univ., Belfast, Ire.). *Structure Properties Thin Films, Proc. Intern. Conf. Bolton Landing, N.Y.* 1959, 495–502.—The decompn. of NH_3 to N_2 and H_2 on thin evapd. films of Ni and Fe were studied at 440° and 417°, resp., by using mass spectrometric analyses. In the case of Ni, activity decreased as the mass of the film increased from 1 to 12 mg. but remained const. for heavier films. The behavior of Fe films tends to be erratic but activity increases monotonously with film wt. Differences between Ni and Fe film data may be correlated with their resp. sintering behavior. Frederick C. Nachod

36. Chem. Abstr. 56, 10968i, 1962.

Reaction before the catalyst during the decomposition of ammonia. Dim. Vladov and Sh. Dinkov. *Godishnik Sofiiskiya Univ. Fiz. Mat.* 54, No. 3, 113–23(1959/60)(Pub. 1961).—Gaseous NH_3 contg. <0.2% H_2O was passed at a velocity of 8–30 cm./sec. through an externally heated quartz tube contg. either a Fe–Al–K catalyst or an inert packing, both at 470°. The gas temps. in the vol. before and after the active catalyst were lower than when an inert packing was used; the temp. difference (ΔT) was greater before than after the catalyst. If a new, nonactivated catalyst was used, ΔT generally increased with time, up to 502 min. These results show that the NH_3 decompn. on the catalyst is a chain reaction proceeding in the ammonia vol. at a linear velocity greater than the exptl. gas velocity.

1960

37. Chem. Abstr. 54, 12756d, 1960.

Catalytic decomposition of ammonia on evaporated metal films. S. R. Logan and C. Kemball (Queen's Univ., Belfast, Ire.). *Trans. Faraday Soc.* 56, 144–53(1960).—Decompn. of mixts. of $NH_3 + H_2$ on metal films was followed by use of a mass spectrometer. Activation energies and pressure dependences were detd. for Ni, Co, Rh, Pt, Ru, and Re. Fe was reported earlier (*CA* 53, 3858*b*). Nitrides formed with V and to varying extents with W and Ta. V nitride was shown by x-ray diffraction to be nonstoichiometric VN, for which some kinetic results were obtained. Reliable measurements were not obtained for Ta nor for Pd, but an activation energy was found for W. Sintering appeared to occur with all metals as they were heated in the presence of the gases to the reaction temp. Only Ni and Fe were investigated in detail. The rate-detg. step of the decompn. was the desorption of N_2 from the catalyst surface, and the results were discussed in relation to theories put forward (*CA* 35, 7273°, 36, 3080°, 42, 2501*g*). Victor R. Deitz

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1961

3. Chem. Abstr. 56, 963g, 1962.

Adsorption phenomena under conditions of ammonia synthesis. A. I. Krasil'shchikov and L. G. Antonova (State Inst. Nitrogen Ind., Moscow). *Zhur. Fiz. Khim.* 35, 1710–15(1961).—An investigation was made of the electrochem. adsorption potential of N_2 on Fe, Ag, and Cu at 425° and on Ni and Cu at 250°, of H_2 on Co at 250° and on Fe at 425°, and of a N_2–H_2 mixt. on Fe at 425° and on Co at 250°. Measurements were made of the potential of a porous metal film in an atm. of the gas, with a Ag-air electrode as the reference. The pos. sign of the potential for the N_2–Fe system (which was higher than in the case of other metals) indicated that the adsorption of N_2 on Fe was accompanied by a transfer of an electron from Fe to N_2, apparently yielding N_2^-. The results show that the rate of formation of NH_3 on Fe was detd. by the adsorption rate of N_2, and the rate of NH_3 decomposition was detd. by the rate of desorption of N_2. The adsorption potential of N_2 on Ni and Co at 250° was approx. −0.15 v. and −0.4 v., resp. The adsorption potential of the N_2–H_2 mixt. lay between the corresponding values for the individual components of the mixt. The potential of Ag at 425° had the same value as at 200° (Antonova, *et. al.*, *CA* 55, 13125*h*).

A. P. Kotloby

. Chem. Abstr. 56, 8518e, 1962.

Study of chemisorption by the kinetic method. (A preliminary note). Miklos Magyar (Vegyipari Egyetem, Fizikai-Kemai Tanszek, Veszprem, Hung.). *Magyar Kem. Folyoirat* 67, 460–1(1961).—A method is described by which the chemisorption of solid-gas reactions can be detd. manometrically. The method is illustrated by the chemisorption of NH_3 during catalytic decompn. with catalysts f activated C contg. Pt, Pd, and Fe oxide in a static system.

Ernest J. Breda

. Chem. Abstr. 55, 24141d, 1961.

Conversion anomaly in small-scale fluidized beds. Pál Szolcsányi (Univ. Chem. Ind., Veszprém, Hung.). *Magyar Kém. Folyóirat* 67, 78–82(1961).—The catalytic (Fe) decompn. of NH_3 was studied in isothermal reactors of 15–30-ml effective vol. and 1.7 and 2.4 sq. cm. in crossectional area, resp. The output of the fluidized bed was higher than that of the stationary bed. The difference was max. at the mean reaction rate/feed rate ratio and decreased when decreasing amts. of catalyst were used. At the onset of fluidization the output increased sharply with an increase in feed rate; on further increase in feed rate, it increased gradually until a max. was reached, and then gradually decreased. The anomaly was attributed to the particle-size distribution and movement of the bed (*CA* 54, 14808*f*). If gaseous voids progressed through the bed at high speed, the gaseous component content increased. Generally, the output at the transitional region was greater when it was approached from the fluidized-bed side than when it was approached from the stationary-bed side.

G. J. Ernyei

1962

41. Chem. Abstr. 58, 7421c, 1963.

Determination of the equilibrium constant of the dissociation reaction of ammonia in a broad interval of temperatures and pressures. P. M. Kessel'man and A. G. Tabachnikov. *Inzh.-Fiz. Zh., Akad. Nauk Belorussk. SSR* 5, No. 10, 19–25(1962). In the general case, K_p is a function of pressure and temp., and only in the limiting case for low values of pressure does it agree with the classical equil. const., K_p, detd. by the law of mass action and depending only on the temp. The literature gives data of various investigators on the calcn. of the equil. const. of the reaction for the synthesis of NH_3, but these data are cited for only a limited temp. interval, and generally include only exptl. values of K_{pa}, where K_{pa} is the equil. const. corresponding theoretically to the gaseous state of the components. For the detn. of K_p as a function of temp. it is sufficient to have accurate data of molar heat capacities of the involved components in a wide range of temps. and also the value of K_{pa} at some one temp. The heat capacities of each component should be known to an error of not more than 0.3%. The difficulty of obtaining the heat capacity of each component acc. to this degree of accuracy is avoided by obtaining an anal. expression for the change of heat capacity during the reaction. For the reaction $NH_3 \rightleftharpoons \frac{1}{2}N_2 + \frac{3}{2}H_2$ this expression is $\Delta C_{pa} = -4.63 + 0.53(t/100) - 0.01235(t/100)^2$, where ΔC_{pa} is $C_{pa}^{NH_3} - \frac{1}{2}C_{pa}^{N_2} - \frac{3}{2}C_{pa}^{H_2}$, and t is the Centigrade temp. The final equations for the equil. const. K_{pa} and the heat of reaction ΔH_0 take the form $\log K_{pa} = -3.107013 \log T + 0.653269 \times 10^{-3}T - 0.045014 \times 10^{-6}T^2 + (2075/T) + 3.389$ and $\Delta H_0 = -9489 - 6.169906T + 2.9874 \times 10^{-3}T^2 - 0.4117 \times 10^{-6}T^3$, where T is the abs. temp. Values of the equil. const. $K_{pa} = p_{NH_3}/p_{N_2}^{1/2}p_{H_2}^{3/2}$ are tabulated for 100° intervals from 200 to 3000°. At 200° K_{pa} is 0.5784, at 1000° 0.0136 × 10^{-3}, at 2000° 0.0133 × 10^{-3}, and at 3000° 0.0586 × 10^{-6}.

William C. Ruehsamen

42. Chem. Abstr. 60, 4843b, 1964.

Structure of commercial Fe catalyst under NH_3 decomposition. I. Determination of phases appearing and their lattice parameters. Toshiji Matsui and Isamu Toyoshima. *J. Res. Inst. Catalysis, Hokkaido Univ.* 10(2), 105–29(1962). Constituent phases and lattice parameters were detd. by x-ray and electron diffraction with catalysts at 3 points on the hysteresis loop of rate of steady decompn. of NH_3. Effects are revealed by decreasing and then increasing H inflow rate, N_H, stepwise at a fixed inflow rate of NH_3, N_A, over doubly promoted Fe catalyst maintained at approx. 450°. At point $N_H/N_A = 0$ the catalyst consisted solely of γ'-phase except just at the inlet of the catalyst bed where a small amt. of ϵ-phase coexisted with γ'-phase. On the upper curve of the hysteresis loop at point $N_H/N_A = 1$ on decreasing N_H the catalyst was solely α-phase, except at inlet of bed, where some γ' coexisted with the main α-phase. On the lower curve, also at $N_H/N_A = 1$ but with increasing N_H, the catalyst was composed solely of γ'-phase or α-phase at the inlet or outlet, resp., with both phases coexisting in the middle. The N content at least at point $N_H/N_A = 0$ decreased along the the line of flow of the catalyst bed. Electron micrographs of surfaces of catalysts exhibited "pore" and "crack" structures, and indicated that pore is only an intergranular void. Surface features of single crystals of Fe in surface of bed were much different from those of catalyst with respect to "pore" structure. Therefore, the promoter in the catalyst inhibits surface migration of Fe atoms.

Arthur Levy

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1963

. Chem. Abstr. 58, 13183a, 1963.

Activation heats for ammonia decomposition on catalysts of ferent chemical natures. I. Catalyst based on iron. Yu. N. Tyurkin, M. T. Rusov, and O. A. Strel'tsov. *Kinetika i Kataliz* 4, 134–8(1963). Activation energies with four different catalysts were detd. as follows: Catalyst compn. in % FeO, %Fe_2O_3, %Al_2O_3, %K_2O, %CaO, %SiO_2, E in kcal./mol., temp. range: 25.16, 74.58, 0.26, —, —, —, 65, 325–475°; 25.12, 75.66, 0.26, 1.96, —, —, 67, 350–560°; 29.20, 64.67, 3.98, 2.15, —, —, 54, 275–475°; 32.13, 58.80, 5.76, 0.87, 3.40, 1.03, 53, 250–300°.

H. K. Zimmerman

. Chem. Abstr. 59, 3346f, 1963.

Catalysis on single crystals. III. Decomposition of ammonia on different crystal surfaces of copper. Joachim Voelter and Manfred Schoen (Deut. Akad. Wiss., Berlin-Adlershof, Ger.). *Z. Anorg. Allgem. Chem.* 322, 202–11(1963); cf. *CA* 54, 9466*c*. The decompn. of NH_3 on disk-shaped single crystals of Cu and on polycryst. Cu is inhibited 1st-order. The greater inhibition on (100) than on (111) faces is attributed to preferential adsorption of H on the (100) face, and is paralleled by a faster anodic dissoln. of the (100) face on electropolishing. The decompns. on the (111) face at 850 and 770° are 2 and 12 times faster, resp., than on the (100) face. The activation energies are 35 and 77.5 kcal./mole on the (111) and (100) faces, resp., and 52.4 kcal./mole on polycryst. Cu. The causes of these effects are discussed in terms of electronic, geometric, and other factors.

Richard H. Jaquith

. Chem. Abstr. 58, 8435a, 1963.

Further shock-tube studies by infrared emission of the decomposition of ammonia. T. A. Jacobs (California Inst. of Technol., Pasadena). *J. Phys. Chem.* 67, 665–7(1963). The decompn. of shock-heated NH_3 was studied by monitoring the infrared emission of the 2.7–3.2-μ fundamental region. The decompn. follows kinetic law given by $d(NH_3)/dt = k(NH_3)^{1/2}(Ar)^{1/2}$, with $k = (2.5 \times 10^{13})e^{-77,700/RT}$ l./mole-sec. Cf. *CA* 57, 11894*d*.

. Chem. Abstr. 59, 14622d, 1963.

Catalytic inhibition of adsorbed hydrogen. S. R. Logan (Univ. Leeds, Engl.). *J. Chem. Educ.* 40(9), 473–4(1963). The catalytic decompn. of NH_3 at several hundred degrees is thought to occur by progressive stripping of H atoms from the adsorbed NH_3 mols., to give adsorbed N atoms that occupy most of the surface of the catalyst. The desorption of these strongly-bound adsorbed atoms, e.g. $2N(ads.) \rightarrow N_2(g)$, is the rate-controlling step, all the other surface processes being in equil. The rate of decompn. is given by: Rate $= k_d \exp(h\theta_N) = k_d(a_0K)^{h/f}(p_{NH_3}{}^2/p_{H_2}{}^3)^{h/f}$, where k_d, a_0, h, and f are consts., θ_N is the fraction of the surface occupied by N atoms, and K is the equil. const. for $2NH_3 \rightleftharpoons N_2 + 3H_2$. An increase in the H_2 pressure alters the surface coverage and diminishes the concn. of the species participating in the rate-detg. step. Thus, the resulting decrease in the rate of decompn. and the neg. exponent in the rate equation are not caused by the preferential adsorption of another species, e.g. H, as previously thought.

James F. Read

1964

47. Chem. Abstr. 60, 12698b, 1964.

NH_3 adsorption on metal promoted catalyst systems. R. T. Barth and R. N. Pinchink (Gulf Res. & Develop. Co., Pittsburgh, Pa.). *J. Phys. Chem.* 68(3), 655–7(1964). The vol. of NH_3 adsorbed on Al_2O_3-and SiO_2-supported Ni, Co, Pt, and W catalysts was measured at 175 and 515°.

R. A. Horne

48. Chem. Abstr. 62, 64f, 1965.

Transient species observed in the catalyzed decomposition of ammonia. Charles E. Melton and Paul H. Emmett (Oak Ridge Natl. Lab., Oak Ridge, Tenn.). *J. Phys. Chem.* 68(11), 3318–24 (1964)(Eng). A research mass spectrometer was used to study the catalytic decompn. of NH_3 over a Pt wire at 10^{-4} to 1 mm. and 75–1300°. Three free radicals, N, NH, and NH_2, were observed in the gas phase and, hence, must have desorbed from the surface of the catalyst. The radical NH_2 was studied *vs.* temp. In addn. to the radicals, the ions NH_4^+ and NH_2^- were observed in the gas phase. These ions were apparently produced by the hot surface of the catalyst; no ionizing electrons were utilized in their production. NH_4^+ was observed at catalyst temps. as low as 500°. NH_3D^+ was obtained from an NH_3D^+ mixt. The activation energy for NH_3 decompn. from a 1:5 H–NH_3 mixt. is 52 kcal./mole of NH_3. Measurable quantities of N, NH, and NH_2 were found in the gas phase when an iron filament was used as a catalyst at 1000°.

RCKG

1965

49. Chem. Abstr. 63, 7688d, 1965.

Kinetics of the decomposition of ammonia on iron catalysts under the conditions of chemical equilibrium. Yu. I. Pyatnitskii, N. A. Stukanovskaya, and V. A. Roiter. *Ukr. Khim. Zh.* 31(3), 244–52(1965)(Russ). A circulating NH_3-synthesis reactor using a doubly promoted Fe catalyst was pumped out and refilled with mixts. of various compns. enriched with $^{15}NH_3$. There was a rapid decrease of $^{15}NH_3$ in the gas stream which was attributed to a rapid equil. with adsorbed N which had not been pumped off the catalyst: 2N (adsorbed) + $3H_2 \rightleftharpoons 2NH_3$ (gas phase). If the catalyst had been in contact with ^{15}N, then after pumping off there was a rapid increase of $^{15}NH_3$ after refilling with ordinary NH_3. Based on the changes of $^{15}N^{14}N$ ratios, the vol. of adsorbed N (expressed throughout the article in terms of the vol. of NH_3 that it would produce) could be calcd. and used to calc. the sum of the vols. of NH_3 in the gas phase and of adsorbed N (V_{NH_3}) and the 2 rate consts., W, in ml./hr.-ml. of catalyst, and k_T, in atm.$^{0.5}$/hr., using $W = \{V_{NH_3}\ln[(Z_0 - 0.38)/(Z_t - 0.38)]\}/t$ and the Temkin-Pyzhev relation (*CA* 34, 6512^7) $W = k_T(p_{NH_3}{}^2/p_{H_2}{}^3)^{0.5}$, Z_0 and Z_t = at. fraction ^{15}N at times 0 and t, 0.38 the final at. fraction ^{15}N. Values of W at equil. calcd. from values of k_T detd. at below equil. conditions were too large. The activation energy for decompn. of NH_3 was 61.5 and 48.5 kcal./mole at equil. and nonequil. conditions, resp. These effects were attributed to the catalyst having its active centers differently coated with the products of the reaction under the 2 sets of conditions. The stoichiometric no. of 2 obtained by Enomoto, *et al.* (*CA* 49, 15437*h*) resulted from their failure to take into account the initial rapid exchange with the catalyst. The method of Bokhoven, *et al.* (*CA* 54, 837*a*) which gave a stoichiometric no. of 1 is more accurate. The rate limiting step is, as assumed by Temkin and Pyshev and by Bokhoven, the adsorption of N. The vol. of adsorbed N fits the relation $0.00174\ T \log a_0P_N$ with $a_0 = 1.095 \times 10^7$, 1.975×10^6, 4.903×10^5, 1.174×10^5 at 375°, 402°, 425°, and 450°, resp.

John Howe Scott

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1965 (continued)

. Chem. Abstr. 63, 12371e, 1965.

te rate-determining step of ammonia synthesis and decomposition over singly and doubly promoted iron catalysts. Kazunori Tanaka (Hokkaido Univ., Sapporo, Japan), Osamu Yamamoto, and Akio Matsuyama. *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964* 1, 676–87, discussion 687(Pub. 1965)(Eng). A new method for deciding the rate-detg. step of NH_3 synthesis or decompn. is presented which is applicable to the case where the overall reaction is more or less apart from equil. The method consists in measuring the stoichiometric no., ν_r, of the rate-detg. step or in directly finding out elementary steps which are in partial equil. By the method presented the detn. of ν_r and the finding of partial equil. are conducted concurrently in a single run of expt. The method was applied to singly and doubly promoted Fe catalysts. The results so far obtained indicate that N chemisorption or desorption is rate-detg. at around atm. pressure and at temps. near 400°. RCTT

Chem. Abstr. 64, 11914f, 1966.

The rate determining step of ammonia synthesis and decomposition. I. Reaction over singly promoted Fe catalyst at 305 and 340°. Kazunori Tanaka (Hokkaido Univ. Sapporo, Japan). *Res. Inst. Catalysis, Hokkaido Univ.* 13(2), 119–50(1965)(Eng). A kinetic investigation was made of NH_3 synthesis and decompn. by the use of ^{15}N as tracer over a singly promoted Fe catalyst at a total pressure of 550 mm. Hg and at 305 and 340°. During the catalyzed NH_3 synthesis or decompn., the chemisorbed N was in partial equil. with the gaseous NH_3 but not with the gaseous N_2. The N chemisorption and desorption were rate-detg. for catalyzed NH_3 synthesis and decompn., resp. In decompn., the observed values for V_r (the stoichiometric no. of the rate-detg. step) were near to unity with reference to the overall reaction, $3H_2 + 2NH_3$, providing further evidence for N_2 desorption being rate-detg. In synthesis, the observed V_r values were appreciably greater than unity and decreased to zero with increasing chem. affinity. This peculiar behavior of V_r can be explained as resulting from the adsorption of NH_3 on the catalyst and the walls of app. during the NH_3 synthesis or decompn.

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Chem. Abstr. 65, 3059f, 1966.

Heterogeneous-homogeneous mechanism in the catalytic decomposition of ammonia. Experiments under static conditions. D. Vladov and Vl. Dyakovich. *Godishnik Sofiiskiya Univ. "Kl. Okhridski," Khim. Fak.* 58, 157–64(1963–64)(Pub. 1965)(Bulg). The decompn. of NH_3 on Pt-Rh and Fe catalysts is a reaction with a heterogeneous-homogeneous mechanism. The amt. of heat Q which was introduced in the reaction was greater than that necessary for the decompn. of NH_3 (Q_2), the heat release, and the heat radiation. The heat was removed from the catalyst by certain active particles. The differences $Q - Q_2$ for the active and the deactivated catalyst were detd. for the % of the decompd. NH_3. B. Hadzija

1966

53. Chem. Abstr. 65, 9786e, 1966.

Catalytic activity of iron-nickel catalysts as a function of their electronic structure. R. F. Lavrentovich, M. T. Rusov, and Yu. N. Artyukh. *Kinetika i Kataliz* 7(3), 553–6(1966)(Russ). The catalytic activity of the Fe-Ni catalyst was detd. by the flow method at atm. pressure and 550–670°. The working medium was a stoichiometric N-H mixt. contg. 23–5% by vol. NH_3. Plots were made of sp. catalytic activity of the Fe-Ni catalyst at 650° and the no. of unpaired *d*-electrons as a function of the catalyst compn. For catalysts of the compns. 100, 80, 70, 65, 55, 45, 35, 30, and 20% Fe, the values of the sp. surfaces and activation energies of NH_3 decompn. were, resp.: 6.3 and 54, 4 and 53, 3.9 and 50, 3.2 and 52, 2.9 and 50, 2.6 and 52, 1.8 and 51, 1.9 and 51, 1.6 $m.^2/g.$ and 52 kcal./mole. The electron work function was detd. for the catalyst under conditions close to those for NH_3 decompn. The contact potential difference of the Fe-Ni catalyst in a N-H-NH_3 atm. at 420° decreased as the Ni content increased, which was analogous to the behavior of the sp. surface with compn. changes. The data presented indicate that the magnitudes of the sp. catalytic activity and the contact potential differences as manifestations of the surface properties of the alloys studied should be closely related with the vol. electronic structure of the alloys, particularly with the no. of unfilled *d*-orbitals. HSJR

54. Chem. Abstr. 67, 26150g, 1967.

26150g The catalytic decomposition of ammonia. VI. Inhibition of decomposition rate. Miklos Magyar, Bela Szenyi, and Janos Mosoni (Hung. Oil Gas Res. Inst., Veszprem). *Veszpremi Vegyip. Egyet. Kozlem., A* 10(1–2), 11–20(1966)(Hung); cf. *CA* 61: 7750a. The decompn. kinetics of NH_3 on a carrier-free Fe oxide catalyst was studied under static conditions at various initial NH_3:H_2 ratios to establish the inhibiting effect of H on the reaction rate. The pressure did not affect the sorption equil., i.e., the apparent activation energy, in the pressure range studied (270–383 atm.). The inhibiting effect of H decreased with increasing temp. owing to an increase in H recombination rate, facilitating the liberation of active centers. The usual 1:3 N:H ratio in industrial NH_3 synthesis is not the optimum one.

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55. Chem. Abstr. 64, 17065d, 1966.

Temperature and concentration distribution in a packed-bed reactor. Y. Oki, E. Oshima, H. Inoue, and S. Yagi (Univ. Tokyo). *Kagaku Kogaku* 30(4), 341–8(1966)(Japan). A computational model was developed for predicting the temp. and concn. distribution in a packed-bed reactor. The model is based on the discontinuous change of temp. and concn. from one void space to another. The mass and heat transfer caused by fluid mixing are represented by the perfect model, which was proposed by Deans and Lapidus, and the other heat transfer mechanism, independent of fluid mixing, is expressed in terms of the stage-to-stage heat transfer coeff. derived from the heat transfer model given by Yagi and Kunii. The catalytic decompn. of NH_3 by an Fe catalyst was carried out, and the rate equation of this reaction was derived from the differential reactor analysis, and then the conversion and temp. distribution in the integral packed-bed reactor of the same reaction was obtained exptl. Calcn. of this reaction and of the oxidn. of SO_2 (Smith, *et al.*) by this new computational model gave better agreement to the exptl. data than the results of other calcn. methods. Cf. Y. K., *CA* 52 11*a*.

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